Zinc oxide has unique properties that make it attractive for a variety of electronic and electro optical applications. Recent technological advances for zinc oxide thin film deposition, along with the availability of production-worthy deposition tools, should create new opportunities for zinc oxide based devices.

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ZnO thin films by MOCVD

Zinc oxide (ZnO) is a II-VI semiconductor material, with a bandgap energy of 3.3eV. The high-bandgap energy puts it in the general class of wide-bandgap semiconductors, which includes gallium nitride (GaN), silicon carbide (SiC) and zinc selenide (ZnSe). Of these, GaN has received the most attention recently, particularly in the areas of blue/ultraviolet lasers and light emitting diodes (LED's).

ZnO eyes the GaN niche

However, ZnO has several important properties that could change this [1]. Similar to GaN, ZnO is a direct bandgap semiconductor which means lasers could potentially be made from the material.

The 3.3eV (375nm) bandgap energy of ZnO puts it in the blue to ultraviolet range of interest for sensor and data storage applications. With suitable alloying, the bandgap of ZnO can be tuned to specific emission values. Zinc oxide has a very high exciton binding energy (60meV), which could potentially make it the brightest emitter of the common wide bandgap semiconductors.

ZnO also has an excellent lattice match to GaN, making ZnO an attractive substrate material (or even an active component) for GaN based devices. ZnO deposits at a much lower temperatures than either GaN or SiC. Large area substrates are readily available for ZnO. In addition, it is radiation hard and high temperature resistant.

The hexagonal (wurtzite) structure allows exploitation of ZnO anisotropic properties when prepared in highly oriented or single crystal forms. It is also a piezoelectric material, with a high coupling coefficient. This has led to surface acoustic wave device development based on ZnO film for communication and sensing applications.

ZnO films can also be prepared with high electronic conductivity (most easily for n-type conducting material.) Since the bandgap of ZnO is well above the visible range, films can be prepared that are electrically conductive, but visibly transparent, leading to applications for transparent conducting oxides (TCO's) and as transparent electrodes for displays and solar cells.

A major obstacle to the commercial use of ZnO films has previously been a lack of reproducible processes to deposit p-type material. This is changing rapidly. The availability of both n- and p-type conducting ZnO films now enables fabrication of p-n junction devices, such as transistors, LED's and diode lasers.

This makes the integration of a variety of functions possible on the same substrate using ZnO, including logic, light emission and light detection components. Economic production of ZnO based LED's and lasers may be possible, as well as visibly transparent transistors and solar-blind ultraviolet detectors.

Deposition of ZnO film

Thin films of ZnO have been deposited by a variety of techniques, including sputtering, evaporation, sol-gel processing, pulsed laser deposition, spray pyrolysis, molecular beam epitaxy (MBE) and metal organic chemical vapor deposition. (MOCVD). All have been used to make ZnO films for applications such as TCO's. For applications in which epitaxial films are required, MBE and MOCVD are preferred, for their ability to control interface chemistry and the deposited film quality.

For depositing ZnO films on large area substrates and at high volume, sputtering or MOCVD are preferred. The combination of excellent film property control

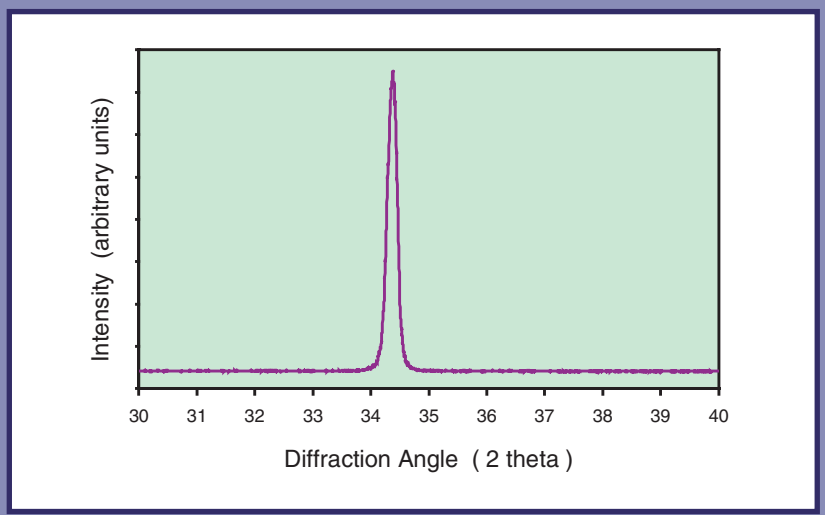

Figure 1 X-ray diffraction results for an epitaxial ZnO film deposited by MOCVD on sapphire at Cermet Inc. The diffraction data was obtained using Copper K alpha radiation.

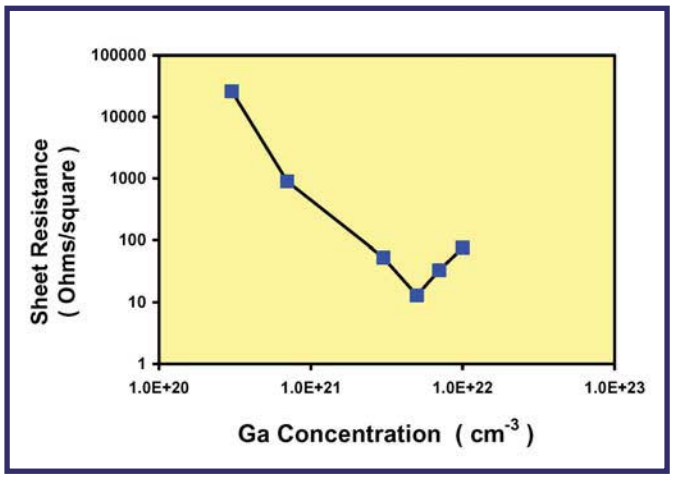

Figure 2: Resistivity of MOCVD deposited gallium doped ZnO thin films versus material composition.

Figure 3: Prototype display devices fabricated with ZnO transparent conducting oxide coatings on the glass faceplates.

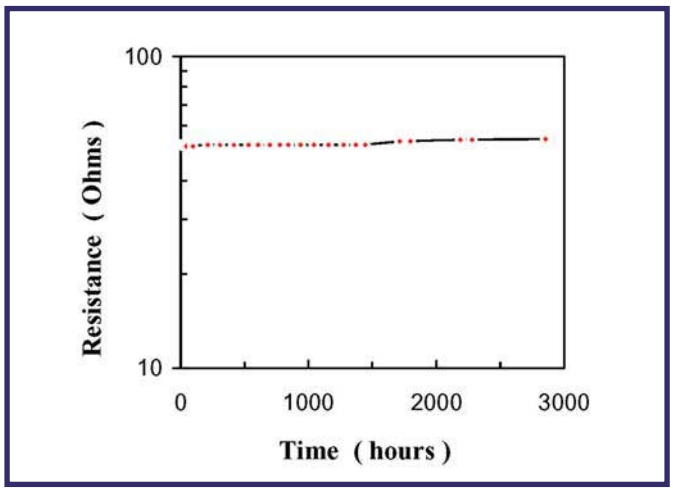

Figure 4: Resistivity versus time for a ZnO film doped with gallium.

and compatibility with high volume production (as well as excellent step coverage over topography) makes MOCVD particularly suited for commercial ZnO device development.

ZnO compatibilities

MOCVD of ZnO is typically done using diethylzinc (DEZn) or dimethylzinc (DMZn) precursor and oxygen. Undoped ZnO films typically behave as n-type, due to defects that act as donors, such as zinc interstitials or oxygen vacancies.

Higher conductivity n-type ZnO films are readily obtained by doping with donor elements that substitute on zinc sites, such as aluminum, gallium or indium, or donor elements that substitute on oxygen sites, such as fluorine.

The p-type ZnO is produced by doping with acceptor elements that substitute for oxygen. Nitrogen is the most commonly used p-type dopant, although phosphorous and arsenic doping has also been reported. Doping ZnO with group IA elements such as lithium, sodium or potassium typically results in semi-insulating films, instead of the p-type behavior that might be expected.

Alloying ZnO with divalent elements such as magnesium or cadmium can be done to enable bandgap engineering. $Zn_{1-x}Mg_xO$ films have a bandgap that increases with x, while the bandgap of $Zn_{1-x}Cd_xO$ films decrease with x. The ability to build multilayer structures of ZnO with $Zn_{1-x}Mg_xO$ and $Zn_{1-x}Cd_xO$ films is useful for fabricating heterojunctions and quantum well devices.

Magnesium and cadmium additions also alter the ZnO index of refraction, and enable fabrication of optical waveguide structures in ZnO based films.

With properly engineered MOCVD technology, ZnO films can be deposited that meet the requirements for a variety of device applications. The critical control parameters for optimum properties are film composition and crystalline texture. Control of film thickness, uniformity and production throughput is also essential for economic device production.

An MOCVD system has been developed at Structured Materials Industries (SMI) specifically for ZnO film deposition. The system provides excellent control of substrate temperature, film growth rate and interface quality, and can deposit ZnO films with crystalline textures ranging from polycrystalline, to highly oriented to fully epitaxial. Accurate and reproducible control of film composition is provided for, in order to deposit doped or alloyed ZnO films with predictable electrical properties.

The MOCVD system can also deposit multilayer films, with composition profiles ranging from graded interfaces to abrupt junctions, depending on the device requirements. Unwanted contamination is minimised, to avoid unintentional compensation and achieve successful p-type doping of ZnO. The system also provides for excellent film uniformity, compatibility with large substrates, high throughput and compatibility with optical monitoring.

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We gratefully acknowledge David Look at Wright State University for the ZnO photoluminescence and Hall measurements. The work is supported in part by the US Department of Energy, under SBIR Phase II Contract No: DEFG02-02ER 83527.

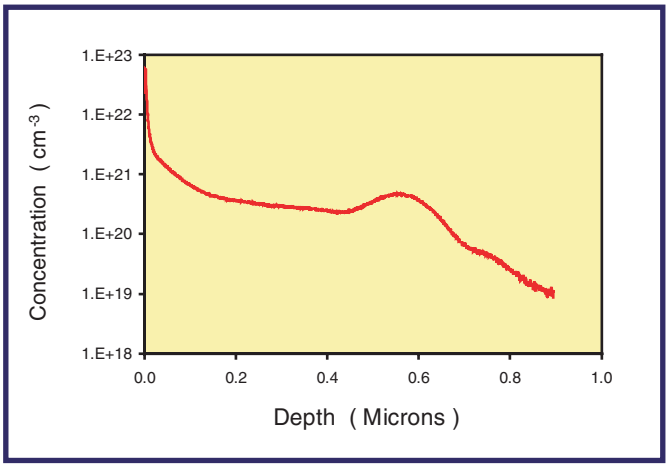

Figure 5. Secondary ion mass spectroscopy (SIMS) results for a nitrogen doped ZnO film deposited by MOCVD at Cermet Inc. Nitrogen is a commonly used p-type dopant for ZnO.

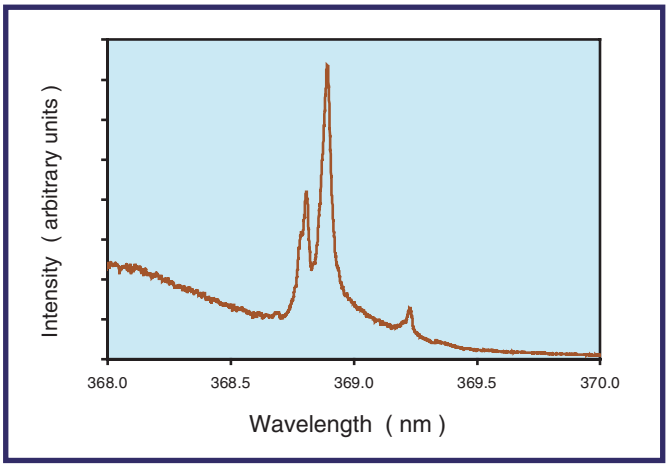

Figure 6: Photoluminescence results for a homoepitaxial ZnO film deposited by MOCVD at SMI. The narrow peak width indicates a high quality ZnO film.

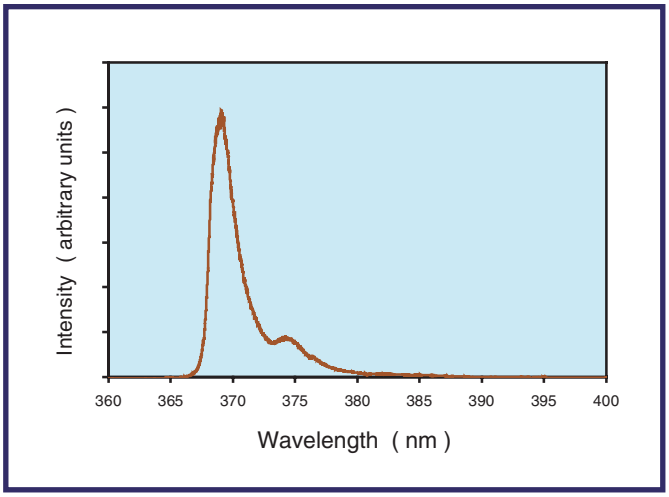

Figure 7: Photoluminescence results for a p-type ZnO film deposited by MOCVD at SMI. The photoluminescence results are consistent with a nitrogen acceptor level in the ZnO film.For p-type films, the photoluminescence results are consistent with a nitrogen acceptor level in ZnO.
Hall measurements of MOCVD deposited p-type ZnO films show carrier concentrations up to 4x1018cm^{-3}, mobilities up to 8.3cm^2/V-s and bulk resistivities down to 7.7ohm/cm.

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